

The Desorption of Gases from Molecularly Plane Glass Surfaces

DISSERTATION

Submitted to the Board of University Studies of
The Johns Hopkins University in Conformity
with Requirements for the Degree of
Doctor of Philosophy

by

JAMES CURRY

Baltimore

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THE DESORPTION OF GASES FROM MOLECULARLY PLANE GLASS SURFACES

Previous investigators¹ have shown that when non-aqueous vapors were adsorbed on molecularly plane glass surfaces the layer of adsorbed molecules was not more than of mono-molecular thickness. However, as Latham pointed out, the method used did not permit them to determine to just what extent the surface was covered and indeed did not prove definitely that under the conditions used the adsorption of a mono-molecular layer of vapor really did take place. Obviously it would be of interest to determine if there were adsorption and if so, to investigate how much and at what temperature desorption from the glass surface occurred.

In order to measure small amounts of adsorption or desorption it is necessary to measure the change in the pressure in a system that has a large ratio of surface to volume. Past investigators have achieved this experimental condition by using a very large surface, usually powdered glass, glass wool or cover glasses, and measuring the pressure change by means of a sensitive gauge. In all such methods the results are influenced by capillarity and besides there is some doubt as to the exact extent of the surface since in no case is the surface molecularly smooth. It was thought that a very simple apparatus could be designed in which there would be no doubt as to the condition and extent of the surface. It was believed that the best way to achieve this was to obtain a large ratio of surface to volume by using an adsorption bulb in which the volume was very small. In order to obtain this small volume, it was thought that the use of a fine capillary tube afforded the best way, but the use of such a tube would preclude the method used by the above investigators for the production of a molecularly plane surface, i.e., by blowing the bulb in a thoroughly melted piece of glass taking particular pains to exclude all moisture. However, the belief was held that if glass were kept for some time at a temperature somewhat below the temperature of definite softening the surface would become molecularly plane due to the action of the surface tension. Consequently preliminary work was done to find out whether or not this idea was correct.

Preliminary Work

The method used to determine if the surface was molecularly smooth was that of the above mentioned workers so it will not be described in detail. In principle it consists in measuring the pressure-temperature relationship of

¹ Frazer, Patrick and Smith: *J. Phys. Chem.*, **31**, 897 (1927); Latham: *J. Am. Chem. Soc.*, **50**, 2987 (1928).

a vapor at its dew-point. If the intersection of the vapor pressure curve and the Charles law curve is a sharp angle, it indicates that there is no adsorption greater than a mono-molecular layer so the surface is assumed to be molecularly plane.

The apparatus used was essentially like that of McHaffie and Lenher¹ so will not be described. The only difference was in the treatment of the bulb in which the measurements were made. In this case a piece of soda-lime glass was obtained from the stock room and the dust carefully wiped out of it by means of cotton. Then it was washed with alcohol and one end sealed shut so as to form a cylinder. Care was taken not to heat any more of the glass than was absolutely necessary. This bulb was immersed in a Kjeldahl flask partially full of boiling sulfur so that its bottom was just above the surface of the sulfur. The bulb was connected to a trap and this latter to an oil pump. The trap was kept surrounded with solid carbon dioxide in order to keep oil vapors out of the bulb. The sulfur was kept boiling vigorously so that its vapors surrounded the bulb and a vacuum maintained for slightly over four hours. Then after cooling the pump was shut off and air let into the bulb through a tube containing P_2O_5 . The bulb was then sealed to the rest of the apparatus and immediately pumped out.

The vapor used in the measurements was toluene which had been well de-aerated. The pressure-temperature relationship was measured when the temperature was both rising and falling. A slight hysteresis was found but in both cases the intersections of the vapor pressure—Charles law curves were very sharp. From this it can be concluded that the surface of a fresh, unwashed, soft-glass tube is rendered molecularly plane by long heating at a temperature somewhat below its melting point.

Description of the Apparatus

The principle, upon which the determination of the amount of desorption was based, consisted in measuring the gas pressure, as the temperature was raised, in a fine capillary tube by means of an adjustable mercury manometer one side of which formed part of the capillary tube.

A diagram of the adsorption apparatus is given in Fig. 1. It consisted essentially of a 0.10 mm lead-glass capillary tube joined to a 1.0 mm capillary tube by means of a very square joint. Care was taken in making this joint to keep the larger capillary tube very uniform and the result was that mercury could move in it very uniformly and regularly up to 1.0 mm from the square joint. This uniformity also did away with capillary depression, so consequently the mercury stood at the same height in tube A and on the fine capillary side when the pressures above the two columns were the same. The tube leading from the cut-off connected to a leveling arrangement in which all rubber was eliminated. The mercury level in these two vertical tubes was adjusted by the movement of a solid glass rod dipping into the open end of the mercury reservoir. The height of the adsorption apparatus in

¹ McHaffie and Lenher: J. Chem. Soc., 127, 1559 (1925).

relation to the leveling arrangement was such that when a vacuum existed in the apparatus the mercury meniscus was slightly below the cut-off.

The tube A was connected by a soft glass to pyrex seal to traps and a pumping system consisting of a mercury diffusion pump backed up by a Hyvac oil pump. Between the mercury pump and the rest of the system there was a trap which was kept surrounded by solid carbon dioxide, principally to keep oil vapor out of the apparatus. The rest of the system consisted of a McLeod gauge and several bulbs and mercury traps which were used to de-aerate liquids. Between the two pumps there was a stop-cock for the purpose of introducing gases.

The furnace used to heat the apparatus consisted of an iron pipe covered with a layer of asbestos upon which nichrome wire was evenly wound and finally a thick layer of asbestos on the outside. It was arranged so that it could be readily slipped over and removed from the capillary tube and was also adjustable vertically above the zero point. The temperature of the furnace was measured by a chromel-alumel thermocouple connected to a portable potentiometer. The movement of the mercury meniscus was followed by means of a carefully leveled cathetometer capable of reading to 0.03 mm.

From the dimensions of the apparatus it is seen that if the mercury is kept at the zero point the ratio of surface to volume in the fine capillary is about 200 and a rough calculation shows that if a mono-molecular layer of a gas is desorbed at 300°C while the volume is kept constant the pressure increase will be about 8 mm and this would be shown by a rise of this height in the mercury in tube A. Thus it is seen that the apparatus is quite sensitive to desorption.

The ratio could have been increased greatly by bringing the mercury up into the fine capillary tube; but preliminary work had shown that experimental difficulties prevented this procedure. In practice the bottom of the furnace was about 1.0 cm above the mercury meniscus at the zero point and under such conditions the vapor pressure of the mercury did not interfere seriously.

After the apparatus was completed it was sealed to the system and the furnace lowered as far as possible. It was then pumped out to a pressure of less than 10^{-6} mm and heated for two hours while the temperature rose

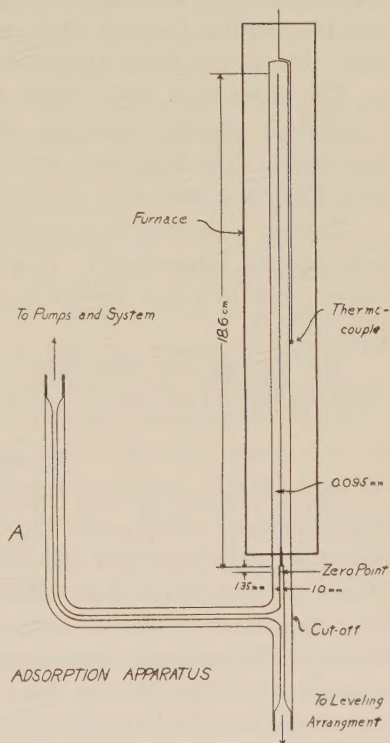


FIG. 1

gradually to 300°C , then during the next two hours the temperature was allowed to rise to 400°C . At this point the pumps were turned off and air allowed to enter the system through a tube containing P_2O_5 . The temperature was kept between 400°C and 425°C for six hours and then the system allowed to cool slowly. The preliminary work had been with soda-lime glass and since the capillary tube was of lower melting lead glass it was thought that the above treatment was ample for the production of a molecularly plane surface and the results obtained later verified this. After this treatment great care was taken not to allow any moisture to get into the system.

The gases used, their source and method of drying are given below:

Carbon dioxide, hydrogen, ethylene and ammonia were obtained from iron tanks. The first three were dried by passing them through a tube filled with P_2O_5 ; the ammonia was passed through a tube of calcium oxide.

Carbon monoxide was made by dehydrating formic acid by means of concentrated sulfuric acid. It was passed through soda-lime and stored over water. Before it was allowed to enter the apparatus it was passed through a tube of P_2O_5 .

The toluene was some that had been dried over P_2O_5 and was de-aerated until the partial pressure of air in it was less than 10^{-4} mm.

Experimental Procedure

The procedure followed in an experiment was the following. The adsorption apparatus was pumped out for several hours at 340°C by means of the diffusion pump and then allowed to cool with the pumps still in operation. When the temperature had fallen to about 75°C the pumps were shut off and in a short time the gas to be studied was allowed to enter the apparatus by means of the previously mentioned stop-cock until the pressure was about one atmosphere. Then the gas was pumped out until the pressure was less than 0.01 mm; this flushing-out process was repeated three times and the gas finally allowed to remain in the system at a pressure of 760 mm. The apparatus was allowed to stand in this condition for varying lengths of time and then pumped out for three-quarters of an hour by means of the oil pump alone. Sometimes the capillary tube was surrounded by solid carbon dioxide during the pumping-out period; when this procedure was used, the pump was not started until the cooling agent had been in position for twenty minutes and in addition the cooling mixture was adjusted so that a reading could be made while it was in place.

The manipulation of the apparatus was quite simple. After the pumping period was over, the mercury was raised above the cut-off (see Fig. 1) so that the meniscus came exactly to the zero point. From the dimensions of the apparatus it was calculated that due to compression the pressure in the capillary was 5.8 times what it was at the end of the pumping-out period. Under experimental conditions this pressure was about 0.10 mm when the meniscus was at the zero point. With the meniscus at the zero point the height of the meniscus in tube A, was read; then the mercury was lowered

about one mm while the capillary tube was heated; then at various temperatures, after standing half an hour or longer, the meniscus was brought up to the zero point and the increase in height noted on the other side. Three readings were made at each temperature and the mean recorded; they checked within 0.10 mm.

The temperature was never raised much above 325°C due to the possibility of the capillary tube collapsing. In some cases after the last reading at the highest temperature the furnace was turned off but the mercury not lowered. Then a reading was taken in the morning and recorded.

Since part of the volume (that just above the mercury meniscus) was not in the furnace it was necessary to find its temperature for different furnace temperatures. This was done by putting a thermocouple in contact with the exposed portion and finding its temperature as that of the furnace was raised. These values were plotted to assist in the calculations. When the furnace temperature was 330°C the temperature of the exposed portion was 120°C.

Since the mercury at the zero point did not remain at room temperature it was necessary to run a blank in order to obtain the necessary corrections to apply to the readings observed when a gas was being desorbed. To do this the apparatus was given the usual preliminary pumping-out at 340°C and in addition was pumped out by means of the diffusion pump for two hours at room temperature before a reading was made. Then the usual readings were taken as the temperature was raised. When the temperature had reached 330°C the mercury was lowered and the apparatus thoroughly pumped out by means of the diffusion pump for an hour and a half and then the mercury raised and another reading taken. The two readings checked within 0.10 mm indicating that the slight pressure increase noticed had not been due to desorption of a gas. At 330°C the value of the blank was 0.45 mm. This blank experiment was made several times and the average values at the different temperatures plotted against the corresponding furnace temperatures.

Results

When the above procedure was followed the data given below were obtained.

TABLE I

No. 1: Air, 10 hrs. P.P. 0.011 mm.

Temp.	T. S.	O. R.	C. P.	m*
25°C	.5	0.06 mm.	0.0 mm.	0×10^{13}
100	.5	1.0	.85	6
235	.5	1.5	1.10	7
315	.5	1.8	1.25	7
315	1.0	1.9	1.35	7

TABLE I (Continued)

Temp.	T. S.	O. R.	C. P.	m*
No. 2: Carbon dioxide, 14 hrs. P.P. 0.011 mm.				
25°C	.5	0.07mm.	0.0mm.	0×10^{13}
120	.5	0.7	0.50	4
205	.75	1.7	1.35	9
290	.75	2.6	2.10	12
298	1.0	2.55	2.05	11
No. 3: Carbon dioxide, 35 hrs. P.P. 0.018 mm.				
25°C	.5	0.1mm.	0.0mm.	0×10^{13}
100	.5	0.9	0.7	5
190	.5	1.5	1.15	8
315	.75	2.25	1.65	9
315	2.75	2.90	2.30	12
310	4.0	2.90	2.30	12
No. 4: Toluene, at 27 mm. for 13 hrs. P.P. (0.017)				
25°C	.5	0.1mm	0.0mm.	0×10^{13}
105	.5	0.55	0.35	3
210	.75	1.35	0.95	6
315	.5	1.85	1.25	7
315	2.0	1.80	1.20	7
305	4.0	1.90	1.30	7
Morning		0.60	0.50	4
No. 5: Ammonia, 10 hrs. P.P. 0.02mm.				
25°C	.5	0.12mm.	0.0mm.	0×10^{13}
120	.75	1.6	1.35	10
212	1.5	1.95	1.55	10
325	1.5	2.45	1.80	10
No. 6: Ammonia, 17 hrs. P.P. 0.04 mm.				
25°C	.5	0.22mm.	0.0mm.	0×10^{13}
105	.5	1.5	1.15	9
220	.75	2.75	2.20	14
320	.75	2.95	2.15	12
No. 7: Hydrogen, 18 hrs. P.P. 0.008 mm.				
25°C	.5	0.05mm.	0.0mm.	0×10^{13}
120	.5	1.0	0.85	6
220	.75	1.45	1.1	7
320	.75	1.40	0.90	5
320	1.25	1.40	0.90	5

TABLE I (Continued)

No. 8: Hydrogen, 16 hrs. P.P. 0.02 mm.

Temp.	T. S.	O. R.	C. P.	m*
-78°C	.5	0.09mm.	0.0mm.	0×10^{13}
25	1.0	3.30	3.2	27
120	.5	5.8	5.55	40
215	.5	6.0	5.40	36
310	.75	6.15	5.55	32
Morning		2.20	2.10	18

No. 9: Hydrogen, 16 hrs. P.P. 0.036 mm.

Temp.	T. S.	O. R.	C. P.	m*
-78°C	.5 hrs	0.15mm.	0.0mm.	0×10^{13}
25	1.5	2.9	2.7	23
200	.5	6.2	5.7	39
300	.5	6.3	5.6	33
340	1.0	5.7	4.9	27
Morning		1.9	1.7	14

No. 10: Hydrogen, 111 hrs. P.P. 0.007 mm.

Temp.	T. S.	O. R.	C. P.	m*
-78°C	.5 hrs.	0.03mm.	0.0mm.	0×10^{13}
25	1.0	1.85	1.8	15
120	1.0	4.15	4.00	29
220	.5	5.4	5.1	33
325	.5	5.5	5.0	28
325	1.0	5.2	4.7	26
330	2.0	4.9	4.4	24
330	3.0	4.75	4.25	24
Morning		2.6	2.55	22

No. 11: Carbon Monoxide, 12 hrs. P.P. 0.006 mm.

Temp.	T. S.	O. R.	C. P.	m*
-78°C	.5 hrs.	0.03mm.	0.0mm.	0×10^{13}
25	1.0	2.3	2.25	20
120	.5	3.4	3.25	24
200	.5	3.85	3.55	24
330	1.0	3.6	3.1	18
Morning		1.2	1.15	10

No. 12: Carbon Monoxide, 16 hrs. P.P. 0.007 mm.

Temp.	T. S.	O. R.	C. P.	m*
-78°C	.5 hrs.	0.03mm.	0.0mm.	0×10^{13}
25	1.0	1.6	1.55	13
105	.5	3.15	3.00	23
200	.5	3.65	3.35	22
325	.1	4.35	3.85	22
325	.5	4.05	3.55	20
325	1.5	2.9	2.4	14

TABLE I (Continued)

No. 13: Carbon Monoxide, 68 hrs. P.P. 0.008 mm.

Temp.	T. S.	O. R.	C. P.	m*
-78°C	.5 hrs.	0.04mm.	0.0mm.	0×10^{13}
25	1.0	1.7	1.65	14
115	.5	3.7	3.55	25
200	.5	5.1	4.8	32
315	.5	5.6	5.1	29
315	1.5	4.4	3.9	23
315	2.0	3.5	2.15	18
Morning		2.2	2.15	18

No. 14: Ethylene, 15 hrs. P.P. 0.015 mm.

Temp.	T. S.	O. R.	C. P.	m*
25°C	.5 hrs.	0.09mm.	0.0mm.	0×10^{13}
120	.5	0.9	0.7	5
205	.5	1.2	0.85	6
325	.75	1.35	0.75	4
325	1.5	1.3	0.7	4
Morning		0.3	0.3	2

No. 15: Ethylene, 15 hrs. P.P. 0.01 mm.

Temp.	T. S.	O. R.	C. P.	m*
-78°C	.5 hrs.	0.06mm.	0.0mm.	0×10^{13}
25	1.0	1.45	1.4	12
130	1.0	2.6	2.4	17
200	1.0	3.2	2.9	19
320	.5	3.4	2.85	16
325	1.25	3.0	2.45	14
340	1.5	3.1	2.5	14
Morning		0.8	.75	6

The number of hours following the name of the gas in Table I gives the length of time that the gas was allowed to stand in the apparatus before it was pumped out. The value following P.P. indicates the pressure at the end of the pumping-out period, i.e. just before the mercury was raised above the cut-off. The temperature is that of the furnace. Where the initial temperature is -78°C it means that the capillary tube was surrounded by solid carbon dioxide while it was being pumped out and then a reading taken under those conditions. The figures under T.S. give the length of time in fractions of an hour that the furnace was kept at the temperature in question before a reading was taken. The values listed under the heading O.R. show the height in mm. that the mercury column rose while the temperature rose from the initial value to the value in question. The value for O.R. at the lowest temperature was obtained by multiplying P.P. by 5.8 (ratio of volumes before and after compression).

The rise observed in the mercury column in tube A as the temperature is increased is the result of three influences, (1) the increase in thermal pressure of the molecules present originally in the gas phase, (2) the change due to the increase of the vapor pressure of the mercury, (3) desorption of molecules and the increase in thermal pressure of molecules desorbed at lower temperatures.

The magnitude of (1) is small since the original pressure was always about 0.10 mm. and it can be calculated from the original pressure and the temperature of the exposed and covered parts of the adsorption apparatus. (2) is found from the results of the blank experiment. Applying these corrections the values listed under C.P. (corrected pressure) show the increase in pressure that is due to desorbed molecules. The next column, m^* , gives the number of molecules which correspond to the pressures listed under C.P. and of course these figures give the total number of molecules that had been desorbed up to and including the temperature in question. The way m^* increases shows the amount of desorption that takes place as the temperature is raised.

In order to calculate m^* it was assumed that all the volume in the furnace was at the furnace temperature and all the exposed portion was at the temperature as determined by the thermocouple put in contact with it. This latter assumption is undoubtedly not quite correct but since this exposed volume occupied such a short length it is quite justifiable. Using these temperatures and the respective volumes as calculated from the dimensions of the capillary tube and the corrected pressures, m^* was calculated for each temperature.

From the observed pressures and the size of the capillary tube a calculation shows that in some cases the mean free paths of the molecules are larger than the diameter of the tube and one might think that the phenomenon of thermal transpiration would cause a complication in the calculations. However, when this was calculated it was found that it would change m^* by much less than the experimental error so it is not of any importance.

In order to calculate the precision of m^* it is necessary to take into account the magnitude of the error in O.R., the blank, the temperature, the pressure of the molecules originally present and the volume of the adsorption apparatus. Estimating all these as fairly as possible it comes out that the percentage error in m^* is 25% when C.P. is 1.0 mm., and 15% when C.P. is 2.0 mm. and for higher pressures it is 10%.

Discussion of Data

Since the way desorption took place for the individual gases is plainly shown by the way m^* changed with temperature it will not be necessary to go into a detailed discussion of the results for each experiment. Consequently only the more important things will be mentioned for each gas and finally a summarizing table will be given.

Air.—Desorption was practically complete by 100°C and further heating at higher temperatures caused no more change. Of course from this experi-

ment alone it is impossible to tell if nitrogen or oxygen was the desorbed gas. In the work presented here it was not planned to study mixtures and this experiment was made essentially for orienting purposes.

Carbon dioxide.—Desorption seemed to be continuous up to 300°C so there is nothing to indicate that the glass surface was free of carbon dioxide at that temperature. In the second experiment, where the gas had stood in the apparatus over twice as long, the desorption at the higher temperatures seemed to take place a little more slowly but the total amount desorbed at 300°C was the same in both cases. It should be noted that a final heating of four hours at this temperature caused no further change.

Toluene.—This had been allowed to stand in the apparatus at a pressure of 27 mm. Since P.P. could not be measured it was assumed to be of the magnitude of the other experiment, since the pumping was the same as usual. The desorption seemed to be gradual and even in amount up to 250°C where it was complete. Keeping the temperature at 300°C for six hours caused no change whatever. The morning reading, which of course was at 25° , indicated that not quite half the molecules had been re-adsorbed. This last point will be discussed later.

Ammonia.—For this gas the second experiment, for which the time of standing was slightly longer and the initial pressure slightly higher, showed that the maximum desorption took place at a higher temperature and was a little larger in amount than for the conditions of the first experiment.

Hydrogen.—The data and the summarizing table show the main features of interest. Of course when the capillary tube was surrounded with solid carbon dioxide the amount of desorption was larger. One striking thing, that first became noticeable with this gas, is that at the higher temperatures there was an actual decrease in the number of molecules present. That is, when the temperature was increased the pressure did not increase as much as it should, and indeed in some cases after standing some hours at a high temperature the pressure was actually less than it had been previously. Since this phenomenon was encountered with other gases its explanation will be postponed until later. In some cases the desorption seemed to be reversible but it was not at all clean cut. In this connection it must be remembered that the morning reading was always at 25° . The results obtained when hydrogen was allowed to remain in the apparatus seven times as long as usual showed that, although the maximum desorption was slightly changed, there was no great difference in the behavior.

Carbon monoxide.—There is nothing in particular to be emphasized here. Long standing seemed to raise the minimum temperature and the amount of maximum desorption as well as to decrease the reversibility somewhat.

Ethylene.—The only unusual point to be noted here is that at the higher temperatures there was a decrease in pressure at first but on long standing it came to a constant value.

For purposes of comparison and for recapitulation of the above statements Table II has been compiled.

TABLE II
Temp. of 25°C

Exp.	14	1	7	4	5	6	2	3
Gas	C ₂ H ₄	Air	H ₂	C ₇ H ₈	NH ₃	NH ₃	CO ₂	CO ₂
S.	15 hrs	10	18	13	10	17	14	35
P. P.	.015mm.	.011	.008	.017	.020	.040	.001	.018
M. T.	205°C	150	150	250	120	220	300*	300*
M. M.	6 × 10 ¹³	7	7	7	10	13	12	12
F.	.32	.20	.20	.48	.24	.31	.36	.36

Temp. of -78°C

Exp.	15	12	11	13	10	9	8
Gas	C ₂ H ₄	CO	CO	CO	H ₂	H ₂	H ₂
S.	15 hrs	16	16	68	111	16	16
P. P.	.010mm.	.007	.006	.008	.007	.036	.020
M. T.	200°C	105	120	200	220	200	120
M. M.	19 × 10 ¹³	23	24	32	33	39	40
F.	1.0	.76	.80	1.0	.94	1.1	1.1

T.S and P.P. have the same meanings as before. M.T. (minimum temperature) refers to the lowest temperature at which desorption was complete. M.M. refers to the maximum number of molecules that have been desorbed up to this temperature. F. refers to the fraction of the surface covered by the molecules desorbed.

In calculating this latter quantity, it was assumed that the desorbed molecules came exclusively from the surface that was entirely in the furnace, this had a magnitude of 0.55 sq. cm. and is 86% of the total possible area. Undoubtedly there was some desorption from the exposed surface but using the above assumption the value calculated will be the maximum possible. The diameter, or sphere of influence, of an adsorbed molecule was calculated from the density of the substances in the liquid state as given in the International Critical Tables. Since the densities are not available for all the substances at 25° and -78° one should not put too much weight on the absolute values listed under F. They only show the order of magnitude and the point to be emphasized is that even taking into account the above mentioned uncertainties there was no evidence that the layer of adsorbed molecules was of polymolecular thickness.

From the table the most striking thing is that for all the gases except carbon dioxide desorption was complete at fairly low temperatures. In some cases this minimum temperature was less than 120° and in only one was it over 220° and this was somewhat doubtful. It should also be added that desorption seemed to take place rather slowly at room temperature but when the temperature was above 150° it took place within about half an hour as a rule.

It appeared that a long saturation period had a slight effect on the subsequent desorption but it varied with the gas. The change was not striking enough to warrant any discussion.

In general, all that can be said as to the reversibility of the desorption is that the apparatus used did not permit careful study. The difficulty is that the conditions under which re-adsorption took place were quite different from the initial conditions of adsorption, particularly in regard to pressure, so one can not really say much about this.

From the data it will be noted that the gases which showed a decrease when kept for some time at the higher pressures were hydrogen, carbon monoxide, and ethylene but this behavior was not noticed with toluene or carbon dioxide. The decrease seemed to be of larger magnitude the higher the temperature and pressure and as mentioned before on very long standing at the higher temperatures it stopped entirely.

There seem to be only two reasonable explanations for this. The first is that at the higher temperatures the glass becomes permeable to some of the gases. This behavior has been well established experimentally but in this case there is no apparent reason why the decrease should finally stop as it did with ethylene. The other suggestion is that at the higher temperatures the mercury becomes permeable to some of the gases. Although this at first seems rather novel there is nothing known either from the standpoint of the properties of mercury or the results obtained with the above gases that is in conflict with this hypothesis. On the other hand there is no positive evidence as yet that mercury does behave in this way.

The above results on the desorption of gases are in accordance with the observations of Sherwood¹ who found that if glass was previously well annealed and then allowed to stand in the atmosphere for some time the gases given off when it was heated again to a temperature slightly below the annealing temperature were true adsorption products and corresponded roughly to a mono-molecular layer. In the above work the temperature never was raised above the preliminary annealing temperature and from the results of the experiments and the blank determinations there was nothing to indicate that there were any gases coming from the decomposition of the glass itself.

Experiments and Results with Water-treated Surfaces

All the work described above has been done in connection with glass surfaces that were molecularly plane and from which moisture had been carefully excluded. Naturally it would be of interest to obtain data on the desorption of water and also to see to what extent the surface of the glass was changed by contact with water vapor. Accordingly experiments were made to determine these points.

In order to do this the adsorption apparatus was allowed to remain for several days open to a bulb of water that had been sealed into the system.

¹ Sherwood: *Phys. Rev.*, **12**, 448 (1918); *J. Am. Chem. Soc.*, **40**, 1645 (1918).

The vapor pressure was that of water at the temperature of the room and was about 25 mm. After this period the adsorption apparatus was pumped out for an hour and a half at room temperature by means of the oil pump and during this time the rest of the system was thoroughly out-gassed by means of a hand-torch. Then an experiment was made in the usual manner and the following data obtained.

No. 16	Water, 62 hours		P.P. (0.017mm)	
	Temp.	T. S.	O. R.	C. P. m*
25°C		.5 hrs	0.10mm	0.00mm 0×10^{13}
110		.4	9.75	9.55 72
210		.15	23.65	23.65 159

It is evident from these figures that water vapor is adsorbed strongly compared to the other gases and vapors used; undoubtedly a change in surface and mechanism of adsorption played an important role in this case.

After the last reading at 210° the apparatus was opened to the diffusion pump for ten minutes; then the furnace was turned off but the pump kept in operation. In an hour when the temperature had fallen to 65° the mercury was raised and a reading taken. Then the furnace was heated to 210° and in fifteen minutes another reading taken. The increase amounted only to 0.40 mm and indicated that practically all the water vapor desorbable at this temperature had been desorbed. The adsorption apparatus was then opened to the diffusion pump and the furnace turned off. When it had cooled to 65° it was opened to the bulb of toluene and flushed out in the usual way. The following results were then obtained.

No. 17	Toluene, 16 hours		P.P. (0.017mm)	
	Temp.	T. S.	O. R.	C. P. m*
25°C		.5 hrs	0.10mm	0.00mm 0×10^{13}
90		.15	0.90	0.75 7
135		.25	1.10	0.85 6
200		.33	5.15	4.80 33

This experiment was identical in all respects to that made before with toluene (No. 4) when the surface was molecularly plane. It will be seen that in this case the desorption up to 120° was slightly higher than that obtained before with toluene, in magnitude it was about the same as that of the previous maximum desorption. From this point on the desorption was very large so the value at 200° was over four times that of the other toluene experiment. It should be noted that the maximum temperature here was slightly lower than the maximum used in the water experiment. This, together with the check made after the previous experiment and the exhaustive pumping would indicate that this large desorption was due to toluene and not to additional water.

After this experiment the system was pumped out and a blank made and then dry hydrogen introduced as usual and the following results obtained.

No. 18	Hydrogen, 17 hours		P.P. 0.007 mm	
	Temp.	T. S.	O. R.	C. P. m*
25°C		.5 hrs	0.13mm	0.0mm 0×10^{13}
110		.15	0.45	0.30 2
200		.33	2.7	2.4 14
300		.33	12.7	11.55 69

This experiment was identical with the first one made on hydrogen (No. 7) except for the intervening water treatment. In this case the desorption at 200° was three times greater than it had been in the previous hydrogen experiment and from the considerations mentioned it is believed that this desorption corresponded to hydrogen and not to water vapor or toluene. In order to see what would happen when the temperature was raised above the maximum attained up to this point it was increased to 300°. The desorption occurring in this interval was very large, in all probability it was mostly water, but perhaps some toluene and hydrogen.

After the last reading at 300° the apparatus was pumped out for half an hour by means of the diffusion pump and then allowed to cool with pumping and again filled with hydrogen.

No. 19	Hydrogen, 17 hrs		P.P. 0.007 mm	
	Temp.	T. S.	O. R.	C. P. m*
25°C		.5 hrs	0.03mm	0.0mm 0×10^{13}
125		.15	0.35	0.15 1
190		.25	0.65	0.40 3
290		.25	1.65	1.20 10
325		.25	4.5	3.60 22

From this experiment it is seen that the desorption up to 200° is much smaller than in the preceding experiment; this is the interval in which the desorbed gas is in all probability hydrogen. In the last three experiments the temperature had never been raised higher than 300° and it is interesting to note that raising it in this experiment to 325° brought about quite a noticeable amount of desorption considering the small temperature interval, this was undoubtedly mostly due to the desorption of water.

By a comparison of the data obtained before and after the surface had come in contact with water vapor the following conclusions seem legitimate.

The water vapor itself is strongly adsorbed and comes off continuously while the temperature is being increased. A second heating through the same temperature range causes no further desorption but heating above the previous maximum temperature brings about more desorption.

After standing in contact with water vapor the glass showed a distinct but not enormous change in surface. Both toluene and hydrogen were adsorbed to about three times the amount on such a surface as on a molecularly plane surface and the desorption did not take place so readily. However,

after additional experiments the amount of desorption diminished, which indicated that the surface was tending to become more and more molecularly plane. This points toward the action of water vapor alone as not being very drastic. It was consideration of this last point that led to the procedure of keeping the apparatus at a high temperature for only a short time. It is not to be expected that water vapor alone would dissolve out part of the glass and change the surface as much as treatment with cleaning solution and subsequent washing with water.

Summary

A simple apparatus has been designed for measuring the desorption of gases from glass surfaces. Its unique features are a very large ratio of surface to volume and the possibility of rendering its surface molecularly plane.

With the surface molecularly plane desorption measurements were made at -78°C and 25°C with the following gases, air, carbon dioxide, toluene vapor, ammonia, hydrogen, carbon monoxide and ethylene.

Measurements were also made after the glass surface had come in contact with water vapor.

BIOGRAPHY

James Rowland Curry was born in Wooster, Ohio, on December 29, 1903, and received his elementary and secondary education in the public schools of that city. He was graduated from Dartmouth College in 1925, having majored in Economics. He studied the usual introductory chemical subjects at that institution during the scholastic year 1926-27. During the summer of 1927 he attended Columbia University and the following fall entered the Graduate School of the Johns Hopkins University. During the year 1929-30 he was the holder of a du Pont fellowship.

